

A Tetrakisstibine Complex of Platinum(II)

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Received September 4, 1976

Although it is thought that stibine ligands should promote pentacoordination for platinum(II) [1], until recently only planar complexes had been isolated in reactions of monodentate tertiary stibines with platinum(II). In a study of the coordination of mixed alkyl-aryl stibines to platinum [2], the pentacoordinate complexes $[\text{Pt}(\text{SbPh}_2\text{Me})_3\text{I}_2]$ and $[\text{Pt}(\text{SbPhMe}_2)_3\text{I}_2]$ have been prepared. It was found that phenyldimethylstibine formed a tetrakis-ligand complex, $[\text{Pt}(\text{SbPhMe}_2)_4\text{Cl}_2]$, which we previously assumed to be four-coordinate. We wish to report a more full investigation of this complex.

Experimental

Physical measurements were obtained as previously described [2]. The complex $[\text{Pt}(\text{SbPhMe}_2)_4\text{Cl}_2]$ was prepared as previously described [2]. *Anal.* Found C, 32.6; H, 3.8; Cl, 5.9. $\text{C}_{32}\text{H}_{44}\text{Cl}_2\text{PtSb}_4$ requires C, 32.5; H, 3.8; Cl, 6.0%.

Preparation of $[\text{Pt}(\text{SbPhMe}_2)_4](\text{ClO}_4)_2$

A solution of the complex $[\text{Pt}(\text{SbPhMe}_2)_2\text{Cl}_2]$ (0.72 g, 1 mmol) in dichloromethane (20 cm³) was stirred with silver(I) perchlorate (0.41 g, 2 mmol) in an inert atmosphere. Acetonitrile (5 cm³) was added, and the mixture was stirred for 20 minutes. The silver chloride was removed by filtration, and the filtrate was stirred with PhMe_2Sb (0.46 g, 2 mmol) for 30 minutes. The solvent was removed by room temperature evaporation and the resulting solid was recrystallised from dichloromethane/ethanol. *Anal.* Found C, 29.3; H, 3.4; Cl, 5.8. $\text{C}_{32}\text{H}_{44}\text{Cl}_2\text{O}_8\text{PtSb}_4$ requires C, 29.3; H, 3.4; Cl, 5.4%.

Results and Discussion

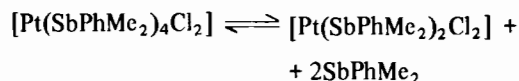
$[\text{Pt}(\text{SbPhMe}_2)_4\text{Cl}_2]$

No $\nu(\text{Pt}-\text{Cl})$ absorption band can be seen in the infrared spectrum of the complex $[\text{Pt}(\text{SbPhMe}_2)_4\text{Cl}_2]$,

suggesting either that it has an ionic structure in the solid state or that it has a tetragonal structure [3-5] with weakly bound chlorine atoms. In view of its behaviour as a nonconductor in nitromethane solution, it is likely that $[\text{Pt}(\text{SbPhMe}_2)_4\text{Cl}_2]$ is tetragonal. Its reflectance spectrum shows a strong absorption at 24.3kK, strongly indicative of planar coordination as would be expected if there were marked tetragonal distortion in the solid state.

The behaviour of this tetrakis-ligand complex in chloroform and dichloromethane solutions is quite complex. The molecular weight in chloroform is 528 (*cf.* calculated value 1182), suggesting that considerable dissociation takes place in solution. It is unlikely that the complex dissociates by loss of chloride ions, since it is a nonconductor in both nitromethane and 1,2-dichloroethane.

A solution of $[\text{Pt}(\text{SbPhMe}_2)_4\text{Cl}_2]$ in CDCl_3 shows a single methyl resonance in the n.m.r. spectrum at 8.89 τ . This signal lies almost exactly half way between those of the bis-ligand complex (8.62 τ) and free ligand (9.19 τ). This could either be coincidental or indicative of a fast exchange reaction between free and coordinated ligand:



Reaction of bis-ligand complex with SbPhMe_2 in 1:2 ratio in dichloromethane produces a solution with identical electronic spectrum to that of the tetrakis-ligand complex. If this reaction is carried out in CDCl_3 , the resulting solution shows a single methyl resonance at 8.89 τ (*cf.* a value of 8.96 τ calculated on the basis of a fast exchange between free and coordinated ligand).

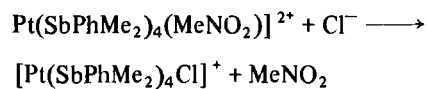
Attempts to freeze this fast exchange reaction by cooling the CDCl_3 solution have proved unsuccessful, there being no change in n.m.r. spectrum on cooling the solution from 34 °C to 70 °C.

$[\text{Pt}(\text{SbPhMe}_2)_4](\text{ClO}_4)_2$

The ionic complex $[\text{Pt}(\text{SbPhMe}_2)_4](\text{ClO}_4)_2$ behaves as a 2:1 electrolyte in $10^{-4}M$ nitromethane solution ($\Lambda_m = 168 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$) and has an electronic spectrum in dichloromethane solution characteristic of planar solution ($\epsilon_{\text{max}} = 32.5\text{kK}$ (sh)). In nitromethane solution, the complex is yellow, *cf.* the colourless dichloromethane solution, and exhibits an absorption at 26.2kK. It seems probable that a molecule of solvent coordinates to the platinum atom giving a pentacoordinate structure.

The conductimetric titration of $2.5 \times 10^{-4}M$ solution of $[\text{Pt}(\text{SbPhMe}_2)_4](\text{ClO}_4)_2$ in nitromethane with a $5 \times 10^{-3}M$ solution of $[\text{Ph}_3\text{PCH}_2\text{Cl}]^+\text{Cl}^-$ shows an end-point after addition of only one

equivalent of Cl^- – a surprising result in view of the existence of $[\text{Pt}(\text{SbPhMe}_2)_4\text{Cl}_2]$. This solution exhibits an absorption at 26.2kK and the chromophore must presumably also be pentacoordinate. The obvious reaction is the replacement of the solvent molecule by a chlorine atom:



Addition of further Cl^- has no effect.

Acknowledgment

I.E.N. is grateful to the Science Research Council for the award of a Research Studentship.

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